

Chemical Reactivity Indexes in Density Functional Theory

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ABSTRACT: The theoretical description of charge distribution, and related properties, such as chemical reactivity descriptors of chemical compounds, has greatly benefited from the development of density functional theory (DFT) methods. Indeed, most concepts stemmed from DFT but, up to now, they have been used mostly within semiempirical MO methods, Hartree–Fock, or post-Hartree–Fock methods. During the last decade, however, DFT has enabled theoretical chemistry to predict accurately structures and energetics of clusters and molecules. Therefore, more attention should also now be paid to these reactivity descriptors determined directly from DFT calculations. In this work, chemical reactivity is explored in DFT through a functional Taylor expansion of energy that introduces various energy derivatives of chemical significance. This review summarizes their main features and examines the limitations of some indexes presently used for the characterization of reactivity. Also, several perspectives are given. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 129–154, 1999

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I. Introduction

The recent impact of density functional theory (DFT) in the development of quantum chemistry is considerable, and can be linked to achievement of so-called “chemical accuracy” at the end

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of the 1980s when gradient-corrected and hybrid functional methods were introduced.^{1,2} Based on the well-known Hohenberg–Kohn theorems,³ DFT focuses on the electron density, $\rho(\mathbf{r})$, itself as the carrier of all information in the molecular (or atomic) ground state. Therefore, the complexity of the problem, becoming limited to a three or four dimensions, is apparently tremendously reduced with respect to the conventional wave function approach, which depends on spatial and spin coordinates.

dinates of all N electrons of the system. Indeed, this is true, but because no accurate density functionals are available for the largest energy term, namely the kinetic energy, the universally used approach

is the Kohn–Sham (KS) method,⁴ which, through the introduction of orbitals, reduces the problem to one in which cost scales formally as the third power of the number of electrons: This is indeed large, but much smaller than the power of four required by Hartree–Fock calculations, and of five, six, or seven by post-Hartree–Fock calculations. (In reality, smaller powers can be obtained for Hartree–Fock and DFT computations, thanks to algorithms and cut-offs in the calculation,⁵ but not for post-Hartree–Fock computations.) In the mean time, DFT programs that exhibit computing time growing linearly in the number of atoms are under development.⁶ The KS method consists of solving Schrödinger Hartree-like equations in which one part of the potential is unknown. There has been much effort made by the chemical physicist community to look for better approximations of this unknown part of the energy functional, namely the exchange-correlation energy, and this is an active area of research (see, e.g., refs. 7–37). The solution of the KS equations leads to the (one-particle) orbitals and, by summation, to the density.

On the other hand, thanks mostly to Parr and coworkers, DFT has been the source of many useful derivations allowing a rationalization of previously ill-defined concepts such as electronegativity, hardness and others until their definition through DFT, as well as developing new concepts. However, due to the prevalence of non-DFT codes in the chemist's world, some of these concepts have been the object of various calculations, mostly through such non-DFT methods as semiempiric models, Hartree–Fock, and post-Hartree–Fock.

The purpose of this work is not to give an exhaustive review of the basis concepts of DFT that have been described extensively elsewhere, but to focus on concepts related to reactivity of molecules, as well as numerical evaluations within the DFT framework. Because the density, $\rho(\mathbf{r})$, contains all information, chemical reactivity should be reflected in its sensitivity to perturbations. After some necessary DFT generalities, gathered in section II, the remainder of the present work is organized as follows:

1. Electronegativity, including electronegativity equalization, and related problems such as charge partitioning will be the subject of the

third section. Hardness and softness will then be discussed, as well as the HSAB principle.

2. Local properties will be the subject of the fourth section, and will include Fukui functions and both local hardness and softness. The relations connecting them and their application to chemical reactivity analysis will be discussed for molecular systems as well as infinite systems.
3. Response functions will be the subject of the fifth section and the relations connecting them to local properties will be discussed, as well as relations between softness kernel, $s(\mathbf{r}, \mathbf{r}')$, response functions, $\chi_1(\mathbf{r}, \mathbf{r}')$, and hardness kernels.
4. Concepts like shape of the electronic density, nuclear Fukui functions, and molecular charge sensitivity analysis will be introduced briefly in the following section.
5. Problems related with the derivative discontinuity of the $E[N]$ functional and the consequences in the usual approximations involved in the determination of the aforementioned properties will be discussed in the seventh section, whereas a scheme allowing one to obtain more accurate electronegativity values will be given.

Finally, some limitations in the present state of the art for the use of these concepts, and the directions into which progress can be expected will be given throughout. Some concluding remarks will focus on the trends and the needs of new calculations to provide further evidence for the usefulness of these concepts in the study of chemical reactivity.

II. DFT Concepts Related to Molecular Charge Distribution

The basis of DFT will not be extensively reviewed here, because this has already been done in many articles and books.^{38–51} Let us just summarize that the Hohenberg–Kohn theorem³ establishes that the ground state of an (electronic) system is just a functional of the (electronic) density, so that, in principle, one only needs knowledge of the density to calculate all the properties of these systems. Splitting the energy functional into kinetic energy, potential energy (i.e., energy from nuclei–electron interaction and energy coming from external fields), classical Coulomb electro-

static repulsion energy, and exchange-correlation energy, E_{xc} (everything else), is a first step in the description of the electronic system.

As already mentioned in the Introduction, the universal exchange-correlation energy functional is unfortunately not known. Moreover, because no accurate kinetic energy functional is presently available, a good estimation of the kinetic energy is practically obtained by the introduction of orbitals in the Kohn–Sham (KS) method. The (small) difference between the true kinetic energy and the kinetic energy calculated from the KS orbitals is rejected in the exchange-correlation functional. The KS orbitals differ from other kinds of orbitals mostly because the sum of the square of the occupied KS orbitals is the true density of the system, whereas a similar sum is only an approximated density in other quantum-chemical methods such as Hartree–Fock. The Kohn–Sham method was introduced in 1965,⁴ and provides solution of the problem through a Schrödinger equation, which differs from the well-known Hartree–Fock equations by the replacement of the exchange potential term with a more general exchange-correlation potential term, which is, in principle, simpler because it is only a function of the density. The spin-orbitals, $\psi_{i\sigma}(\mathbf{r})$, are solutions of KS equations:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right)\psi_{i\sigma}^{ks} = \epsilon_{i\sigma}^{ks}\psi_{i\sigma}^{ks} \quad (1)$$

where the effective potential, V_{eff} , is the sum of the external potential, $v(\mathbf{r})$ (the electron-ion potential plus any other potential applied to the system), the Hartree potential for electrons, $V_H(\mathbf{r})$, and the exchange-correlation potential, $V_{xc\sigma}(\mathbf{r})$. $V_{xc\sigma}(\mathbf{r})$ is the functional derivative, $\delta E_{xc}[\rho_\sigma(\mathbf{r})]/\delta\rho_\sigma(\mathbf{r})$ and $\rho_\sigma = \sum_i |\psi_{i\sigma}|^2$, $\rho = \sum_\sigma \rho_\sigma$ (σ being the spin index). The power of this approach lies in the fact that this latter potential includes not only the exchange in the Hartree–Fock sense, but also the correlation (which is referred to all what is missed by the Hartree–Fock approach), and also the difference between the exact kinetic energy of the system and the one calculated from the KS orbitals.

Therefore, the KS orbitals have a great similarity to the orbitals generated by other *ab initio* or semiempirical methods. Although this has not always been recognized in the past,⁵³ the KS orbitals contain at least as much information as traditional orbitals, because they are computed through a (in principle) better Hamiltonian, which also includes electron–electron correlations. Consequently, KS orbitals can be used with no restriction in theoretical studies of chemical reactivity^{54–56}, for instance,

in frontier orbitals analysis. We will come back to this point later.

For sake of clarity, when not explicitly specified, spin index will be omitted in the following equations, its introduction being straightforward. As we will examine in section IV *E* spin polarization is, however, an essential ingredient in DFT, and should not be neglected in the calculations.

The basis equation of DFT is obtained through the minimization of the energy functional of the electron density, $E[\rho]$, with the constraint of constant number of electrons, N :

$$\delta\left(E - \mu \int \rho(\mathbf{r}) d\mathbf{r}\right) \quad (2)$$

with:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (3)$$

Whereas, in eq. (2), μ is just a Lagrange multiplier, the variational principle leads to the well-known Euler equation:

$$\mu = v(\mathbf{r}) + \frac{\delta F[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \quad (4)$$

In eq. (4), $v(\mathbf{r})$ is the external potential, already defined, and $F[\rho(\mathbf{r})]$ is the energy functional that contains kinetic energy, classical electron–electron Hartree–Coulomb repulsion energy, and exchange-correlation energy, and which is universal according to the Hohenberg–Kohn theorems³:

$$\begin{aligned} E &= \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + F[\rho] \\ &= \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \\ &\quad + E_{kinet}[\rho] + E_{Coul}[\rho] + E_{xc}[\rho] \end{aligned} \quad (5)$$

To get the physical significance of μ , and to introduce other concepts, it is necessary to write some Maxwell-like equations through the total differential expansion of the energy, E , for instance in the change of one ground state to another. E being a functional of the number of electrons and the external potential, $v(\mathbf{r})$ (i.e., $E = E[N, v(\mathbf{r})]$), can be expressed:

$$dE = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} dN + \int \left(\frac{\partial E}{\partial v(\mathbf{r})}\right)_N \delta v(\mathbf{r}) d\mathbf{r} \quad (6)$$

It is identified to the following one, using the fact that E is a functional of the electronic density $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$; that is, $E =$

$E[\rho(\mathbf{r}), v(\mathbf{r})]$:

$$dE = \int \left(\frac{\partial E}{\partial \rho(\mathbf{r})} \right)_{v(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r} + \int \left(\frac{\partial E}{\partial v(\mathbf{r})} \right)_{\rho(\mathbf{r})} \delta v(\mathbf{r}) d\mathbf{r} \quad (7)$$

One should mention that, whether or not eq. (6) is exact, eq. (7) is only approximate, because it assumes that $\rho(\mathbf{r})$ and $v(\mathbf{r})$ are independent, whereas the Hohenberg–Kohn theorems³ demonstrate that $v(\mathbf{r})$ completely determines the ground-state density, $\rho(\mathbf{r})$. This is the origin of some of the ambiguities encountered in sections IV and V in this work. Incorporating, eqs. (4) and (3) into eq. (7), one gets:

$$dE = \mu dN + \int \rho(\mathbf{r}) \delta v(\mathbf{r}) d\mathbf{r} \quad (8)$$

which, by identification with eq. (6), leads to:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\mathbf{r})} \quad (9)$$

μ is therefore a chemical potential, and it has been identified with the negative of the electronegativity ($\chi = -\mu$).⁵⁷

Similarly, one gets:

$$\rho(\mathbf{r}) = \left(\frac{\delta E}{\delta v(\mathbf{r})} \right)_N \quad (10)$$

The energy expansion [eq. (6)] may not be limited to first order.⁶¹ Table I lists the various derivative terms up to third order. In Table I, following ref. 62, derivatives indicated by arrows toward the

left of the table are partial derivatives with respect to the number of electrons N , whereas derivatives indicated by arrows toward the right are partial derivatives with respect to the potential, $v(\mathbf{r})$. It is worth noticing that differentiations with respect to N give a global character to the properties, whereas differentiations with respect to $v(\mathbf{r})$ introduce a local character.

The second-order derivatives terms also have clear physical meanings. The first of them is the second derivative with respect to the number of electrons:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\mathbf{r})} \quad (11)$$

This is a global property that was introduced by Parr and Pearson⁵⁸ in 1983 who gave, for the first time, a precise definition for hardness, a concept vaguely defined at that time, but widely used since its introduction by Pearson⁵⁹ in the 1960s for the rationalization of acid–base reactions. Indeed, Parr and Pearson⁵⁸ introduce an arbitrary 1/2 factor in their definition, which is less and less retained in present works, and which will be omitted accordingly throughout this study. The softness, S , also called global softness (*vide infra* in section IVA) is simply the inverse of the hardness:

$$S = \frac{1}{\eta} \quad (12)$$

The $\chi_1(\mathbf{r}, \mathbf{r}_1)$ term in Table I is the linear response function, and the middle term, $f(\mathbf{r})$, is a mixed term called the Fukui function first defined

TABLE I.
Derivatives of Electronic Energy (Canonical Ensemble).^a

Perturb. order	$E[N, v(\mathbf{r})]_{\tau}$				
$n = 0$	$\frac{\partial}{\partial N}$				$\frac{\delta}{\delta v(\mathbf{r})}$
$n = 1$		μ chem. pot.		$\rho(\mathbf{r})$ density	
		η hardness	$f(\mathbf{r})$ Fukui f.	$\chi_1(\mathbf{r}, \mathbf{r}_1)$ response f.	
$n = 2$		η'	$f'(\mathbf{r})$	$\xi_1(\mathbf{r}, \mathbf{r}')$	$\chi_2(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$

^a Properties become more and more local (global) when going from the left-hand side (right-hand side) to the right-hand side (left-hand side) of the table. Left (right) derivatives are against the electron number, N (potential $v(\mathbf{r})$).

by Parr and Yang⁶⁰ in 1984. These terms will be discussed in section V and IVA, respectively.

The linear response function, $\chi_1(\mathbf{r}, \mathbf{r}_1)$, and further derivatives with respect to the potential, $v(\mathbf{r})$, are density—density response functions of the many-body perturbation theory. Other quantities are all derivatives of the chemical potential and are electronic chemical responses. All of these last quantities are sensitive to the discontinuity of the $E(N)$ function for molecules and systems possessing a HOMO–LUMO gap. This point will be discussed in section VII. Third-order terms (i.e., second-order perturbation responses) can also be derived, and we refer the reader to the work of Senet for an examination of their properties within a solid-state physics approach.^{61,62}

The finite temperature ensemble description in DFT⁶³ has greatly helped to understand concepts such as hardness and softness, thanks to Parr and coworkers.^{64,65} Table I lists their definitions within the canonical ensemble from the energy functional, $E[\rho] = E[N, v(\mathbf{r}), T]$, whereas Table II offers the definitions of reciprocal functions as derivatives of the grand potential functional, $\Omega[\rho] = \Omega[\mu, v(\mathbf{r}), T] = E[\rho] - N\mu$, within the grand canonical ensemble. $\Omega[\rho]$ satisfies the definition relation of a hardness functional introduced by Parr and Gázquez.⁶⁶ Relations connecting these functions are given in subsequent sections.

Defining chemical reactivity as the series of derivatives of electronic density with respect to electron numbers or chemical potential limits our description of the reactivity to responses to global perturbations. In a true chemical reaction, however, the electronic density undergoes a local perturbation leading to a nonlocal response. Therefore, second-order derivatives appear more appropriate for this purpose: nonlocal hardness and soft-

ness kernels are therefore the privileged functions for these studies and will be the subject of section V.

III. Global Properties: Electronegativity and Related Concepts

Global properties are characteristics of a molecule or a subsystem as a whole.

A. ELECTRONEGATIVITY

Electronegativity is an old idea originally introduced by Pauling^{67,68} in 1932 that describes the capability of an atom in a molecule to attract electrons. Pauling quantified this concept through thermodynamical arguments relating bond energies, leading to the idea of property scaling as the square root of an energy. A few years later, Mulliken proposed a quite simple definition of electronegativity, namely the arithmetic average of ionization energy and electron affinity, EA ⁶⁹:

$$\chi = \frac{I + EA}{2} \quad (13)$$

This definition leads to a property homogeneous to an energy. Whereas Pauling and Mulliken scales are most frequently used for comparisons of electronegativities of elements, other definitions of electronegativity have also been proposed by Gordy, Allred-Rochow, and Sanderson^{70–72} and many other investigators. We refer the reader to the reviews given in refs. 73–75 for more details on this subject. Pauling's scale is considered by most chemists as the most appropriate scale of electronegativity, although it is less well founded

TABLE II. Derivatives of Electronic Grand Potential (Grand Canonical Ensemble).^a

Perturb.
order (n)

	$\frac{\partial}{\partial \mu}$	$\Omega[\mu, v(\mathbf{r})]_T$	$\frac{\delta}{\delta v(\mathbf{r})}$
n = 0		N elec. nb	$\rho(\mathbf{r})$ density
n = 1	S softness	$s(\mathbf{r})$ loc. softness	$-s(\mathbf{r}, \mathbf{r}')$ softness kernel

^a Properties become more and more local (global) when going from the left-hand side (right-hand side) to the right-hand side (left-hand side) of the table. Left (right) derivatives are against the chemical potential (potential $v(\mathbf{r})$ [in fact $u(\mathbf{r})$, see eq. (60)]).

than Mulliken's. This point will be discussed in section IIIF. One should emphasize that all these scales cannot fit together exactly, because Mulliken's scale is homogeneous to an energy, whereas Pauling's is homogeneous to a square root of energy. The others scale in still different ways (e.g., as forces or other physical quantities) or are dimensionless. Therefore, linear relations between Mulliken's electronegativity and Pauling's proposed in the past^{74,76} cannot be justified theoretically.

Nevertheless, if one admits a linear relationship between Mulliken's and Pauling's scales, the conversion factor must be proportional to a square root of energy, which can be obtained by a contribution of the hardness in this factor. Komorowski⁷⁷ obtained promising results for a collection of bonds and molecules with such a factor, in which the hardness was estimated by the van der Waals radius.⁷⁸

The idea that electronegativity is a chemical potential can be traced back to Gyftopoulos and Hatsopoulos.⁷⁹ Interestingly, Iczkowski and Margrave⁸⁰ also pointed out that the Mulliken definition [eq. (13)] is just the finite difference approximation to a partial derivative of the energy, E , versus the number of electrons. This expression can be obtained in a natural way within the DFT framework, as shown in the previous section, through the identification by Parr et al.⁵⁷ of the electronegativity, χ , to minus the chemical potential, μ [eq. (9)]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right) \quad (14)$$

The concept of orbital electronegativities is rather old (1962),^{73,76} and has recently been discussed by Liu and Parr.⁸¹

B. SANDERSON'S ELECTRONEGATIVITY EQUALIZATION

Sanderson proposed, in the 1950s, the following statement: "When two or more atoms, initially possessing different electronegativity, link to form a compound, their electronegativities become adjusted to a same intermediate value within the compound."⁷² Although he found little success at that time, the principle was proven by Parr in 1978. Politzer and Weinstein showed, in 1979, that the electronegativity of all portions of the total number of electrons in a diatomic molecule are the same.⁸² Indeed, this was unnecessary, because, as

soon as the identification of the electronegativity, χ , with the chemical potential, μ , is admitted (see section II) the chemical potential of a system in equilibrium is the same everywhere! However, an accurate determination of the chemical potential is far from trivial, and this will be discussed in section VIIB. In Sanderson's school, the "intermediate value within the compound" is obtained from a geometric average of the (Sanderson) electronegativity of the constituting atoms in the molecule. Parr and Bartolotti⁸³ justified the geometric average in 1982. Sanderson's electronegativities were derived from a linear relation of the atomic (partial) charge of the atoms. With this method charges within molecules can be estimated, but it suffers from the severe drawback that all atoms of a given element will have the same atomic charge within a molecule (one may think of the oxygens or hydrogens in methanoic acid). The method was later improved by the partial-equalization-of-orbital-electronegativity method introduced by Gasteiger and Marsili.⁸⁴ Their method consists of an iterative scheme performed separately in each bond to evaluate the charge shift. Finally, the electronegativity equalization method, introduced by Mortier and coworkers,⁸⁵ allows for expression of the electronegativity of an atom within a molecule as a linear function of charges within the molecule, and it has been applied successfully to some inorganic systems like zeolites.^{86,87}

All these methods involve the concept of atomic charges in molecules, which are not quantum-mechanical observables. So it is not surprising that charges cannot be derived uniquely by different schemes, and they may lead to quite different values. Among the methods, one can cite: (1) the universally used Mulliken partitioning, which extracts charges from the molecular orbital population analysis; (2) the natural orbital population analysis⁸⁸ (performed with the so-called natural atomic orbitals, which maximize the localization through a diagonalization of the density matrix); (3) the electrostatic-potential-based-charges method^{89,90} (CHELPG, charges from electrostatic potential), widely used in biochemistry; (4) Bader analysis, using topological partitioning of the density⁹¹; or (5) the atomic polar tensor method introduced by Cioslowski.⁹² (For a review of these methods, see Bachrach⁹³ and ref. 90.) In a recent review, Geerlings et al.⁹⁴ tested these different methods for a panel of 15 molecules, at different levels of theory. If an agreement can be observed for the highest levels of theory (hybrid DFT functionals

vs. QCISD in their work⁹⁴), the numbers obtained may vary considerably with the methods. It is to be noted that QCISD can lead to spurious results in some cases; for instance, see ref. 95.

It appears reasonable to consider that reliable electronegativities should be determined directly from the electronic density of the molecule. DFT provides a simple way to do that through relation (14). Indeed, this equation has been used widely, but almost uniquely through its finite difference approximation, namely Mulliken's definition [eq. (13)]. This is indeed not sufficiently accurate for the purpose of getting an absolute value for electronegativity. However, it provides a powerful means for relative comparisons. In practice, most contemporary studies of electronegativities use Mulliken's approximation. This may be a source of the inaccuracy responsible for some of the failure when one applies Sanderson's principle for determination of, for example, charge transfers. We will return to this point in subsection VII B.

C. HARDNESS AND SOFTNESS

As mentioned in the second section, hardness, η , has been defined as the second partial derivative with respect to the number of electrons [eq. (11)] and the (global) softness, S , is simply equal to its inverse [eq. (12)]. Considering the variation in energy when one electron is added or removed from the system (i.e., using a finite difference approximation) one gets:

$$\chi = \frac{I + EA}{2} \quad (13)$$

$$\eta = I - EA \quad (15)$$

$$S = \frac{1}{\eta} = \frac{1}{I - EA} \quad (16)$$

It is recalled that I and EA are the vertical ionization energy and electronaffinity, respectively, in line with the constant external potential requested by the partial derivative [eqs. (9) and (11)]:

$$I = E(N = N_0 - 1) - E(N = N_0) \quad (17)$$

$$EA = E(N = N_0) - E(N = N_0 + 1) \quad (18)$$

N_0 being the number of electrons in the ground state of the (usually neutral, but may be charged) system.

Hardness is favored by a small size of atoms. Before any relation between electronegativity and hardness was recognized, the size of atoms was introduced in the electronegativity definitions (e.g.,

Gordy $[Z/r]$,⁷⁰ Allred-Rochow $[Z/r^2]$,⁷¹ or Sanderson $[Z/r^3]$).

The link between hardness and polarizability was discussed by Komorowski⁹⁶ with atoms modeled by metallic spheres. The polarizability of a metallic sphere with radius r is reasonably approximated by $4\pi\epsilon_0 r^3$. The second derivative of the energy with respect to the charge of the metallic sphere is given by $\eta = (4\pi\epsilon_0 r)^{-1}$ (assuming a frozen constant radius of the sphere within ionization); the electric capacity of the sphere $\sigma = 4\pi\epsilon_0 r$ is accordingly identified to the softness. Reasonable agreement can be found between these theoretical data and experimental data extracted from refraction indices.⁹⁷ Giambiagi and de Giambiagi obtained convincing correlations between softness and molecular polarizability of a variety of molecules,^{98,99} whereas, for neutral atoms, Vela and Gázquez obtained a correlation coefficient amounting to 0.75 between polarizability and softness,¹⁰⁰ which is not as fantastic.

Senet¹⁰¹ recently showed that hardness is exactly for open-shell systems, and approximately for closed shells, the screened (Coulomb + exchange-correlation) interaction between frontier orbitals. The link between hardness and density of states is discussed in section IV C.

Various stable molecules may possess LUMOs with positive energies, which can be measured experimentally by electron attachment spectroscopies (inverse photoemission spectroscopy BIS, XANES, etc.). It has become evident that these values should be used for the determination of electronegativity and hardness within the finite approximation [eqs. (13) and (15)] instead of $EA = 0$ (adiabatic value), as first suggested in early works.¹⁰²

A relationship between energy and global hardness differences was established by Gázquez et al.,¹⁰³ whereas Toro-Labbé et al.¹⁰⁴ established a more general relation between potential energy, chemical potential (i.e., electronegativity), and hardness profile.

Making use of statistical thermodynamics concepts, the chemical system can be identified as a member of a grand canonical ensemble (μ, v, T) ,³⁸ in which softness can be defined in terms of number fluctuations as:

$$S = \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{v,T} = \frac{1}{k_B T} (\langle N^2 \rangle - \langle N \rangle^2) \quad (19)$$

with k_B being the Boltzmann constant, and $\langle \rangle$ designating ensemble averages at constant T, v, μ .

Hardness is defined similarly within the canonical ensemble (N, v, T):

$$\eta = \left(\frac{\partial \langle \mu \rangle}{\partial N} \right)_{v, T} = \frac{1}{k_B T} (\langle \mu^2 \rangle - \langle \mu \rangle^2) \quad (20)$$

D. HSAB PRINCIPLE

"Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties" is the HSAB principle in the earliest form, as suggested by Pearson in 1963.⁵⁹ The largest objection to the principle was that no exact definition of hardness existed at that time, and only relative values of η for series of acids and bases were provided. However, the qualitative relation between the softness and polarizability was established: a high polarizability can allow a large deformation of the electronic cloud, in line with the term *softness*.⁵⁹ When Parr and Pearson gave their definition of chemical hardness,⁵⁸ they also provided a proof of the HSAB principle: Neglecting the external potential perturbation, the chemical potential change in the formation of a diatomic molecule AB can be written as (the superscript "⁰" labeling the properties before formation of the bond):

$$\mu_A = \mu_A^0 + \eta_A^0 \Delta N_A \quad (21)$$

$$\mu_B = \mu_B^0 + \eta_B^0 \Delta N_B \quad (22)$$

Because, once the molecule is formed, $\mu_A = \mu_B$ and $\Delta N_A = -\Delta N_B$, the charge transfer between A and B (at constant external potential) is:

$$\Delta N = \frac{\mu_B^0 - \mu_A^0}{\eta_B^0 + \eta_A^0} \quad (23)$$

B being the species of highest chemical potential (i.e., the Lewis base) and A that of lowest chemical potential (i.e., the Lewis acid). The charge transfer is driven by the electronegativity, whereas the hardness prevents it.

The energy change associated with the formation of AB is:

$$\begin{aligned} \Delta E &= -\frac{1}{2} (\mu_B^0 - \mu_A^0) \Delta N = -\frac{1}{2} \Delta \mu \Delta N \\ &= -\frac{1}{2} \frac{(\Delta \mu)^2}{(\eta_B^0 + \eta_A^0)} = -\frac{(\Delta \mu)^2}{2} \frac{S_A S_B}{S_A + S_B} \quad (24) \end{aligned}$$

At this point, the formation of the molecule AB can be thought of as resulting from two successive

steps, namely:

1. A charge transfer leading to a common chemical potential, μ , which is driven by lowering energy.
2. A reorganization of the charges distribution at constant T and μ , following the hardness principle (*vide infra*).

Splitting ΔE into two contributions, ΔE_A and ΔE_B , with:

$$\Delta E_A = -\frac{(\Delta \mu)^2}{2} \frac{\eta_A}{(\eta_A^0 + \eta_B^0)^2} \quad (25)$$

and maximizing ΔE in eq. (24) with respect to η_A or η_B at constant $\Delta \mu$ leads to $\eta_A = \eta_B$; that is, $S_A = S_B$ —the HSAB principle. More general proofs of the HSAB principle have been given by Parr et al.^{105,106} under the restriction of common chemical potential of the reaction partners (instead of a constant external potential), and Gazqu  z and Mendez¹⁰⁷ later provided a local HSAB principle showing that the interaction between two chemical species occurs mostly through atoms having approximately equal softness (instead of through their softest atom). We will return to the HSAB principle in section VD. Following these concepts, an interpretation of the regioselectivity in Diels–Alder reactions was recently given by Geerlings.¹⁰⁸

The maximum hardness principle, proposed by Pearson^{109,110} establishes that, for equal electronegativity and equal external potential, increasing stability is obtained by increasing hardness. Parr and Chattaraj¹¹¹ gave a proof in 1991, but Sebastian¹¹² showed that the proof was in error. A recent derivation was recently given by Liu and Parr,¹¹³ which, although it was not a proof, offered a favorable view of the maximum hardness principle.

Using this concept, Choho et al.¹¹⁴ concluded that C_{60} is the most stable fullerene, compared with C_{70} , C_{50} , and others. This maximum hardness principle allows for understanding of the shell structures of atoms, molecules, or metal clusters (magic numbers)¹¹⁵ and is also invoked to examine small HOMO–LUMO gaps connected with instabilities or large gaps with stability.¹¹⁶ The application of the maximum hardness principle along a reaction path has been studied recently.^{216,217}

The question of space partitioning to define atoms in molecules is again raised if one wants to

apply Sanderson's principle in connection with the HSAB principle. Komorowski proposed a scheme making use of the Fock, overlap, and bond order matrices to derive electronegativity for bonded atoms.¹¹⁷ Indeed, his scheme does not lead to a proper equalization of electronegativity, because he made use of the mean value [eq. (13)] instead of the correct derivative definition for a given fragment or atom A :

$$\chi_A = - \left(\frac{\partial E}{\partial N_A} \right)_{N_B \neq A} \quad (26)$$

However, his results are quite encouraging, because they lead to a set of values of χ_A exhibiting a linear relation to the Mulliken population, p_A :

$$\chi(p_A) = \bar{\chi}_A + p_A \bar{\eta}_A \quad (27)$$

Such a relation was first proposed by Huheey¹¹⁸ whose standard average electronegativity $\bar{\chi}_A$ was the valence-state electronegativity of free atoms. It was shown that electronegativity of bonded atoms may be significantly different from that of the corresponding free atoms. Such an approach uses space partitioning based on the Hilbert space. Hence, the accuracy will certainly depend on factors such as basis sets, energy functionals, and more generally the quantum model, etc. Topological partitioning should lead to more reliable values, but this has not yet been tested.

According to Klopman,¹¹⁹ soft-soft reactions are frontier controlled (i.e., the frontier orbitals are the reactivity index) and hard-hard interactions are charge controlled (i.e., electrostatic interactions play the essential role). We will see in section VD that these conclusions can be deduced from DFT.

E. GROUP ELECTRONEGATIVITIES AND HARDNESSES

Global properties like electronegativity and hardness can be calculated at different levels of partitioning of the system, and such calculations have been undertaken frequently in organic chemistry for groups such as alkyl, aryl, etc. Usually, these functional groups are considered in calculations as radicals with the geometry they have in the molecules (e.g., pyramidal $\dot{\text{C}}\text{H}_3$). Very good correlations are found between these electronegativities and physical properties like NMR coupling constants.¹²⁰ (Let us recall that this property has been proposed in the past to calibrate the electronegativity scale.⁷³) Geerlings¹²¹ showed very good correlations with electronegativities and

hardnesses calculated from approximations^{13,15} at various levels of *ab initio* theory (i.e., Hartree-Fock and post-Hartree-Fock) for 30 groups. So-called experimental hardnesses were those in Pearson's compilation,^{122,123} which are the differences in experimental ionization and electronic affinity energies according to eq. (15).

Group softness can be similarly defined and related to the capacitance of groups to acquire charge.¹²⁴ Good correlation between polarizability and softness was obtained in ref. 125. Geerlings¹²¹ pointed out that the softness of the substituents was the predominant factor (vs. electronegativity) in the determination of (gas-phase) basicity order in alkylamines. Toro-Labbé et al. recently introduce fragment hardnesses¹²⁶ and correlated reaction energies to changes in chemical potential and hardness.

F. CHARGE TRANSFER WITHIN A BOND

Charge transfer was related to electronegativity differences soon after Pauling's definition, the charge transfer being proportional to the electronegativity differences, and the proportionality constant exhibiting an inverse proportionality to the square root of the bond distance, R_{AB} . Such charges, given by $(\chi'_A - \chi'_B)/R_{AB}^{1/2}$, with χ' being Pauling's electronegativity, are generally in good agreement with charges obtained from quantum-mechanically calculated charges deduced from Mulliken population analyses.

Although Geerlings obtained good correlations between number of transferred electrons and experimental acidities or basicities, eq. (23), which looks more elaborate, leads to poorer estimations of the charge transfer, as shown by Komorowski.⁷⁸ Eq. (23) was modified by Nalewajski by introducing a core polarization energy,¹²⁷ and by Komorowski by incorporating polarization and induction interaction between atoms.⁷⁷ Three major reasons may be suggested to explain the apparent superiority of Pauling's data:

1. The use of the finite difference approximation in the definition of electronegativity in eq. (13).
2. The neglect of spin polarization in the definition [eq. (14)] (this will be discussed in section IVE).
3. Pauling's electronegativity includes the effects of hardness of partners involved in a chemical bond; therefore, the two scales should not be compared.

It would be worthwhile to revisit eq. (23) with numerical data obtained through differentiations instead of finite differences.

IV. Local Properties: Fukui Functions and Related Properties

Local properties may vary from point to point in space and are one-point (\mathbf{r}) functions.

A. FUKUI FUNCTIONS

Local properties are highly desirable in establishing a reactivity-oriented description of molecular systems. Electron density distribution is basic for understanding chemical reactivity, and electrophilic or nucleophilic attacks can be rationalized on the basis of electrostatic interactions. Furthermore, the change in electron density under the influence of an approaching reagent is also of considerable importance. Fukui¹²⁸ first recognized the importance of frontier orbitals as principal factors governing the ease of chemical reactions and the stereoselective path. Parr and Yang^{60,129} demonstrated that most frontier theory can be rationalized from DFT. They defined the Fukui function of a molecule, reflecting the reactivity of a site, as:

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} \quad (28)$$

that is, the change in the electron density driven by a change in the number of electrons, which is, because of the Maxwell relation, identical to the functional derivative of the chemical potential with respect to a change in the external potential (see Table I). Accordingly, it measures the sensitivity of a system's chemical potential to an external perturbation at a particular point. Fukui functions are normalized as one can deduce by integration of eq. (28).

In contrast to hardness or electronegativity, which are global quantities, the Fukui functions are local and reflect the properties of the different sites within the molecule. In principle, a Fukui function needs only the electron density of the neutral species to be calculated, provided a good functional is used. Such an attempt was made by Chattaraj et al.¹³⁰ and Pacios and Gómez.¹³¹

For a molecular or atomic system, the derivative of eq. (28) is discontinuous,¹³² and difficult to evaluate. Consequently, Yang and Parr have pro-

vided three numerical definitions for Fukui functions:

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^+ : \text{governing nucleophilic attack} \quad (29)$$

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^- : \text{governing electrophilic attack} \quad (30)$$

$$f^0(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^0 : \text{governing radical attack} \quad (31)$$

With the same finite difference approximation used for electronegativity and hardness [eq. (18)], the Fukui functions, $f(\mathbf{r})$, can be calculated from differences in density:

$$f^-(\mathbf{r}) = \rho_{(N=N_0)}(\mathbf{r}) - \rho_{(N=N_0-1)}(\mathbf{r}) \quad (32)$$

which is valid when the system undergoes an electrophile attack; that is, it decreases its number of electrons, and from:

$$f^+(\mathbf{r}) = \rho_{(N=N_0+1)}(\mathbf{r}) - \rho_{(N=N_0)}(\mathbf{r}) \quad (33)$$

which is used when the system undergoes a nucleophilic attack (i.e., it increases its number of electrons). The third function, $f^0(\mathbf{r})$, governing radical attack, is estimated as the average of $f^+(\mathbf{r})$ and $f^-(\mathbf{r})$. Different levels of sophistication can be made for such computations, according to the method of calculation of the density (i.e., the orbitals). Most previous works used traditional *ab initio* quantum chemistry, with various levels of sophistication in the treatment of correlation and the quality of basis set.^{133–136} More in line with the involved theory, DFT calculations have been performed recently.¹³⁷

The Fukui functions have been expressed in terms of the KS frontier orbitals, ψ_F , by Yang and Parr^{60,129}:

$$f^\alpha(\mathbf{r}) = \sum_{\sigma} |\psi_F^\alpha(\mathbf{r}, \sigma)|^2 + \sum_{i, \sigma}^{\text{occ}} \left(\frac{\partial |\psi_i(\mathbf{r}, \sigma)|^2}{\partial N} \right)_{v(\mathbf{r})}^\alpha \quad (34)$$

with $\alpha = +, -, \text{ or } 0$ as in eqs. (29)–(31).

Eqs. (32) and (33) may be further approximated through the frozen orbital approximation. In such an approximation, the difference in densities is simply equal to the density of the depleted or

populated orbital through the ionization or electron attachment processes, respectively:

$$\rho_F(\mathbf{r}) = \sum_{\sigma} |\psi_F^{\sigma}(\mathbf{r}, \sigma)|^2 \quad (35)$$

This approximation, also designated as the Koopmans approximation by Cioslowski et al.¹³⁵ assumes that the orbitals of the system remain unchanged upon electron detachment or attachment. One is therefore led to the venerable frontier orbitals approximation, introduced by Fukui in 1952.¹³⁸ It is worthwhile to consider the importance of this last approximation: Figure 1 shows the Fukui functions $f^-(\mathbf{r})$ and $f^+(\mathbf{r})$ of the NH_2OH molecule within the two approximations. One can clearly see (although the contour values have been adjusted to make the two pictures as similar as possible) the relaxation of the electronic density around the oxygen and nitrogen atoms due to the occupation of the LUMO or the depletion of the HOMO. A similar comparison was made by Mendez and coworkers¹³⁹ for maleimine within Hartree–Fock calculations. Langenaeker et al. concluded that the HOMO density was a poor approximation of the Fukui function $f^-(\mathbf{r})$ (Hartree–Fock calculations on substituted benzenes).¹⁴⁰

Geerlings also, concluded from various studies,^{140,141} that the Fukui function and the Laplacian of the charge density are not closely related, as indicated in previous works by Giambiagi et al.⁹⁸

Integral forms for eq. (34) making use of the softness kernel or potential response functions are given in section V. Fukui functions will then be depicted as screened frontier orbitals approximated by the density of frontier orbitals, but only in cases of unpolarizable electrons or noninteracting electrons.¹⁰¹

B. CONDENSED FUKUI FUNCTION

Condensed Fukui functions are numbers obtained by approximate integrations of the Fukui function over atomic regions. Proposed by Yang and Mortier¹⁴² in 1986, these functions depend on the approximation involved in the definition of the atomic region. Furthermore, condensed Fukui functions have been considered to be sensitive to various parameters involved in the calculation such as basis sets, choice of more or less correlated *ab initio* method, correlation functional in case of DFT calculation, numerical integration schemes, etc. (see, e.g., ref. 143). In fact, it has recently been recognized that the choice of the Mulliken population analysis scheme to define the atomic region is mainly responsible for the dispersion of values. This is not surprising, because atomic charges, unlike electron density, and as already mentioned in section IIIB, are not quantum-mechanically observable, and the weakness of Mulliken population analyses in the calculation of charges in polar molecules is well known.¹⁴⁴ Indeed, any property based on population analyses grounded on Hilbert space partitioning should exhibit some unreliability, as shown by Cioslowski.¹⁴⁵ Geerlings^{94,164} concluded that Fukui functions were sensitive to the population analysis method, finding different conclusions for the descriptions of ambident nucleophile anions for different schemes of charge partitioning (Bader analysis, natural orbitals population analysis, and Mulliken analysis). Cioslowski obtained quite reliable estimates of condensed Fukui function through the use of a topological theory of atoms,¹³⁵ although the set of molecules was limited to six. More recently, Gilardoni et al.¹⁴⁷ showed, within 7650 calculations on maleimide with different combinations of basis sets, DFT functionals, and numerical integration grids, that

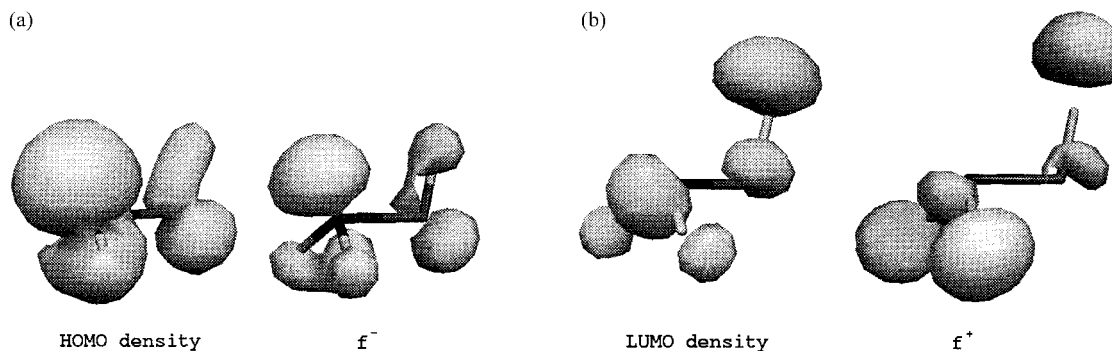


FIGURE 1. Fukui functions and frontier orbitals of hydroxylamine densities NH_2OH (a) f^- (left) and HOMO (right) (b) f^+ (left) and LUMO (right) isocontour values (a.u.) HOMO: 0.01, LUMO: 0.05; f^- : 0.012, f^+ : 0.01.

the condensed Fukui function can be very stable against these parameters if the (topological) Becke numerical integration scheme¹⁴⁸ is used, as it is the case in some DFT codes (to our knowledge, the Becke grid was used in refs. 149–153, whereas similar numerical schemes were used in refs. 154–160).

C. LOCAL SOFTNESS

In 1985, local softness was defined by Yang and Parr¹⁶² as:

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{v(\mathbf{r})} \quad (36)$$

Because global softness was defined [eq. (12)] as:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} \quad (36)$$

one has:

$$S = \int s(\mathbf{r}) d\mathbf{r} \quad (37)$$

and:

$$\begin{aligned} s(\mathbf{r}) &= \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{v(\mathbf{r})} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} \left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} \\ &= f(\mathbf{r}) \cdot S \end{aligned} \quad (38)$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity. Indeed, local softness combines the site reactivity index, $f(\mathbf{r})$, with the global softness measure, S . It can be considered as a distribution of global softness weighted by the Fukui function over the molecule, so that it may be considered as a softness density. Geerlings¹⁰⁸ suggested that local softness should be used as an intermolecular re-

activity index, and Fukui function as an intramolecular index. Thus, the comparisons of Fukui functions or condensed Fukui function values of different systems are meaningless because they represent only the relative reactivity among different sites in a molecule. Therefore, the local softness was qualified by Harbola et al.⁶⁴ as the natural DF concept for characterizing a site. The Fukui function may be obtained from the local softness from eqs. (37) and (38) (but the reverse is not true), and can be thought of as normalized local softness. $s(\mathbf{r})$ is measurable using scanning tunnel microscopy.¹⁶¹

For a gapless system, such as a metal, the number of electrons is given by:

$$N = \int g(\epsilon) \frac{d\epsilon}{1 + \exp(\beta(\epsilon - \mu))} \quad (39)$$

$g(\epsilon)$ being the density of states (DOS), and β being the inverse of the temperature, $1/k_B T$.

For a metal, at 0 K, μ is equal to the Fermi energy, ϵ_F , and the number of electrons N is simply given by:

$$N = \int_0^{\mu} g(\epsilon) d\epsilon \quad (40)$$

so that:

$$\left(\frac{\partial N}{\partial \mu} \right)_{T,V} = S = \frac{1}{\eta} = g(\epsilon_F) + \int_0^{\mu} \frac{dg(\epsilon)}{d\mu} d\epsilon \quad (41)$$

V being the volume, supposed to remain unchanged in the differentiation. This equation may be approximated by:

$$\left(\frac{\partial N}{\partial \mu} \right)_{T,V} = S = \frac{1}{\eta} \simeq g(\epsilon_F) \quad (42)$$

if one neglects the last term. This underlines the general property that metal hardness decreases when the DOS increases.¹⁶² The importance of the last term, omitted in ref. 162, was raised by Cohen.¹⁶³ Indeed, it should not be omitted for small systems; for instance, in case of a metal sphere, one can show that the leading term in the hardness does not contain $g(\epsilon_F)$ and is related to the sphere size.^{101, 164}

Similar to eq. (40), one can obtain the density from the local density of states (LDOS), $g(\epsilon, \mathbf{r})$:

$$\rho(\mathbf{r}) = \int_0^{\mu} g(\epsilon, \mathbf{r}) d\epsilon \quad (43)$$

so that, assuming the validity of eq. (42):

$$\begin{aligned} f(\mathbf{r}) &= \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{T,V} = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{T,V} \left(\frac{\partial \mu}{\partial N} \right)_{T,V} \\ &\simeq \eta g(\epsilon_F, \mathbf{r}) \simeq \frac{g(\epsilon_F, \mathbf{r})}{g(\epsilon_F)} \end{aligned} \quad (44)$$

The Fukui function is the normalized LDOS at the Fermi level [the normalization $\int f(\mathbf{r}) d\mathbf{r} = 1$; eq. (52) corresponds to $\int g(\epsilon_F, \mathbf{r}) d\mathbf{r} = g(\epsilon_F)$].

$$s(\mathbf{r}) = g(\epsilon_F, \mathbf{r}) + \int_0^{\epsilon_F} d\epsilon \left(\frac{\partial g(\epsilon, \mathbf{r})}{\partial \mu} \right)_{v(\mathbf{r})} \quad (45)$$

The leading term is:

$$s(\mathbf{r}) \approx g(\epsilon_F, \mathbf{r}) \quad (46)$$

It was identified independently by Parr and Yang^{38,162} although they omitted the second term in eq. (45), implicitly performing a frozen-orbitals approximation.

According to eq. (46), metals, which exhibit large DOS at the Fermi level, are soft. Their softness values are large, but finite, contrary to the expectation given by the finite difference approximation ($\eta = I - EA$) [eq. (15)]. Chemisorption and catalytic reactions on metal surfaces can be thought of as soft-soft chemical reactions. As for molecules, the Fukui function, $f(\mathbf{r})$, measures the site reactivity for metal surface reaction.¹⁶²

Similar to eq. (20) for the global softness, a fluctuation formula within the grand canonical ensemble can be given for $s(\mathbf{r})$ at finite temperature:

$$s(\mathbf{r}) = \frac{1}{k_B T} (\langle \rho(\mathbf{r}) \cdot N \rangle - \langle \rho(\mathbf{r}) \rangle \langle N \rangle) \quad (47)$$

D. LOCAL HARDNESS

Hardness density, $\eta(\mathbf{r})$, may be defined in a similar manner to local softness; that is, by analogy to eq. (37):

$$\eta = \int \eta(\mathbf{r}) d\mathbf{r} \quad (48)$$

or, by analogy, to eq. (36):

$$\eta(\mathbf{r}) = \left(\frac{\partial \mu}{\partial \rho(\mathbf{r})} \right)_{v(\mathbf{r})} \quad (49)$$

But the functional derivative is ambiguous for a ground state, because the Hohenberg-Kohn theorem establishes that $v(\mathbf{r})$ is completely determined by $\rho(\mathbf{r})$. We will return to this point in section VB.

Nevertheless, this last definition can be combined with eq. (28), so that local hardness and Fukui functions are related through:

$$\eta = \int \eta(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} \quad (50)$$

and an inverse relation is obtained with the local softness [eq. (38)]:

$$\int \eta(\mathbf{r}) s(\mathbf{r}) d\mathbf{r} = 1 \quad (51)$$

This reciprocity equation holds globally, but not locally. Therefore, eqs. (67) and (68), which are

built on the hardness kernel, have to be used (discussed in section V). One can notice that, by substituting eq. (51) into eq. (50), one finds the normalization of the Fukui function, already mentioned after eq. (28):

$$\int f(\mathbf{r}) d\mathbf{r} = 1 \quad (52)$$

An approximate form of the local hardness was proposed by Berkowitz and Parr¹²⁴:

$$\tilde{\eta}(\mathbf{r}) \approx - \frac{V_{el}(\mathbf{r})}{N} \quad (53)$$

where $V_{el}(\mathbf{r})$ is the electronic part of the molecular electrostatic potential:

$$V_{el}(\mathbf{r}) = - \int \frac{\rho(\mathbf{R}) d\mathbf{R}}{|\mathbf{r} - \mathbf{R}|} \quad (54)$$

(where \mathbf{R} s are atom coordinates) and its use was investigated by Geerlings and coworkers.^{137,165}

A third reactivity index, introduced recently by Senet,¹⁰¹ is the screened local hardness (discussed in section VB).

E. SPIN POLARIZATION

For magnetic systems, spin-polarized Fukui function and local softness or hardness functions must be used to correctly describe the system; for example, one has:

$$f_{\sigma}(\mathbf{r}) = \left(\frac{\partial \rho_{\sigma}(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} \quad (55)$$

with $\sigma = \uparrow$ or \downarrow . Misra et al.¹⁶⁶ has shown that spin polarization is of little importance in the calculation of condensed Fukui functions. The importance of spin polarization has in fact been neglected in most calculations of Fukui functions. Indeed, Cioslowski et al.¹³⁵ showed that it is generally small, although some of their calculations failed because of spin contamination. Here, again, the use of DFT-KS calculations instead of Hartree-Fock or MP2 calculations should lead to more reliable results, due in part to the well-established smaller spin contamination obtained in KS calculations.

Although it can be small, spin polarization is essential because it removes the degeneracy that could lead to infinite softness for open-shell systems within frozen-orbitals approximation (be-

cause of the constraint in the “restricted” calculations that forces \uparrow and \downarrow orbitals to be degenerate).

Moreover, one can expect that spin polarization may play a larger role in some cases, for instance, photochemical reactions involving triplet excited states (as suggested by Cioslowski et al.¹³⁵), as well as organometallic compounds involving transition metals. To our knowledge, the first calculation of Fukui function for a metallocene appeared only recently,¹⁴⁷ although the compound studied did not have high spin states.

More fundamentally, within DFT, the total energy is a functional of the independent functions $\rho_{\uparrow}(\mathbf{r})$ and $\rho_{\downarrow}(\mathbf{r})$ instead of $\rho(\mathbf{r})$. Some spin-polarized generalization of the concepts of electronegativity and hardness may be found in works of Ghanty and Ghosh.¹⁶⁷ However, in our opinion, it seems more fruitful to express DFT equations in terms of the total density, $\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r})$ which obeys eq. (3), and the spin density, $\rho_s(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$, which integrates the spin number:

$$N_s = N_{\uparrow} - N_{\downarrow} = \int \rho_s(\mathbf{r}) d\mathbf{r} \quad (56)$$

In terms of $\rho(\mathbf{r})$ and $\rho_s(\mathbf{r})$, the total energy for the system in the presence of the external potential, $v(\mathbf{r})$, and an external magnetic field, $B(\mathbf{r})$, in the z direction is given by:

$$E[\rho, \rho_s, v, B] = F[\rho, \rho_s] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} - \mu_B \int B(\mathbf{r})\rho_s(\mathbf{r}) d\mathbf{r} \quad (57)$$

μ_B being the electron Bohr magneton, and F as defined in eq. (4). With total charge density and spin density being independent functions, one must carry out the minimization procedure by taking into account the energy variation with respect to both. One obtains, in addition to eq. (4):

$$\begin{aligned} \mu_s &= \left(\frac{\delta E[\rho(\mathbf{r}), \rho_s(\mathbf{r})]}{\delta \rho_s(\mathbf{r})} \right)_{\rho, v, B} \\ &= -\mu_B B(\mathbf{r}) + \frac{\delta F[\rho(\mathbf{r}), \rho_s(\mathbf{r})]}{\delta \rho_s(\mathbf{r})} \end{aligned} \quad (58)$$

Standard KS calculations keep a constant spin multiplicity (i.e., the value of N_s), which may not necessarily lead to the true ground state of the system. Similar to eq. (9) for the chemical poten-

tial, one obtains:

$$\mu_s = \left(\frac{\partial E}{\partial N_s} \right)_{N, v(\mathbf{r}), B} \quad (59)$$

which has been called the spin potential—that is, the measure of the tendency of a system to change its spin polarization—from Gálvan and coworkers.^{168,169} Gálvan et al. also introduced spin hardnesses and related Fukui functions.^{168,170} The changes of N_s keeping N constant are associated with the transit through different valence states so that μ_s —a ground-state property—is related to the energies of promoted states.

F. OTHER LOCAL INDICES

Other local reactivity indices may be introduced, taking into account variations with respect to variables not considered in Tables I and II, such as the electron temperature, T , which induces electronic excitations. They will not be discussed here, although one should cite the local isoelectronic reactivity indices recently introduced by Wilke, Cohen, and Scheffler,¹⁷¹ which are shown to be closely related to the local softness.

V. Kernels and Linear Responses

They are two points $(\mathbf{r}, \mathbf{r}')$ functions. Their interest for reactivity studies comes from the fact that local softness and Fukui functions are both defined as responses to a global perturbation, whereas the chemical reaction is typically local.

A. SOFTNESS KERNEL

The softness kernel (also called the charge transfer softness kernel) is defined by:

$$s(\mathbf{r}, \mathbf{r}') = \frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')} \quad (60)$$

$u(\mathbf{r}')$ being defined as $\delta F[\rho]/\delta \rho(\mathbf{r}')$, which is equal to $\mu - \nu(\mathbf{r}')$. The softness kernel integrates to the local softness:

$$\int s(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = s(\mathbf{r}) \quad (61)$$

Using the previously defined quantities, one gets the identities:

$$S = \iint s(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' = \int s(\mathbf{r}) d\mathbf{r} \quad (62)$$

$$s(\mathbf{r}) = f(\mathbf{r})S \quad (38)$$

The corresponding fluctuation formula for the softness kernel is:

$$s(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B T} (\langle \rho(\mathbf{r}) \cdot \rho(\mathbf{r}') \rangle - \langle \rho(\mathbf{r}) \rangle \langle \rho(\mathbf{r}') \rangle) \quad (63)$$

B. HARDNESS KERNEL

The hardness kernel is defined in the same terms as the softness kernel [eq. (60)]:

$$\eta(\mathbf{r}, \mathbf{r}') = -\frac{\delta u(\mathbf{r})}{\delta \rho(\mathbf{r}')} = \frac{\delta^2 F[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (64)$$

$F[\rho]$ is the universal functional of the electronic density, as discussed earlier [eq. (4)], and related to the energy density functional by eq. (5):

$$E[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + F[\rho] \quad (5)$$

A reciprocity relation between hardness and softness kernel exists in a similar way to that between the local and global hardness/softness:

$$\int s(\mathbf{r}, \mathbf{r}'') \eta(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r}') \quad (65)$$

so that hardness and softness kernels are true inverses. The hardness kernel integrates to local hardness, $\eta(\mathbf{r})$, although a weighting function is introduced:

$$\eta(\mathbf{r}) = \int \eta(\mathbf{r}, \mathbf{r}') f_1(\mathbf{r}') d\mathbf{r}' \quad (66)$$

where f_1 can be any normalized function. It may be helpful to take the Fukui function, $f(\mathbf{r})$, or the normalized $\rho(\mathbf{r})/N$ density. From the hardness kernel, one can define the corresponding local hardness:

$$\eta(\mathbf{r}) = \int \eta(\mathbf{r}, \mathbf{r}') \frac{\partial \rho(\mathbf{r}')}{\partial N} d\mathbf{r}' = \int \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}' \quad (67)$$

or:

$$\eta(\mathbf{r}) = \int \eta(\mathbf{r}, \mathbf{r}') \frac{\rho(\mathbf{r}')}{N} d\mathbf{r}' \quad (68)$$

The relation:

$$\int s(\mathbf{r}) \eta(\mathbf{r}) d\mathbf{r} = 1 \quad (51)$$

obtained by substituting eq. (61) into eq. (66) shows that $s(\mathbf{r})$ and $\eta(\mathbf{r})$ are inverse, but this is only a global reciprocity, which is described by eq. (51), contrary to the true reciprocity of the kernels, given by eq. (65) and first derived by Berkowitz and Parr.¹²⁴

The hardness kernel^{124, 172, 173} defines the global hardness by:

$$\begin{aligned} \eta &= \frac{\partial^2 E}{\partial N^2} = \int \int \left[\frac{\delta^2 F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right] \frac{\partial \rho(\mathbf{r})}{\partial N} \frac{\partial \rho(\mathbf{r}')}{\partial N} d\mathbf{r} d\mathbf{r}' \\ &= \int \int \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) f(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (69)$$

which is shown to be equivalent to:¹⁷⁴

$$\begin{aligned} \eta &= \frac{\partial^2 E}{\partial N^2} = \int \int \left[\frac{\delta^2 F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right] \frac{\partial \rho(\mathbf{r})}{\partial N} \frac{\rho(\mathbf{r}')}{N} d\mathbf{r} d\mathbf{r}' \\ &= \int \int \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) \frac{\rho(\mathbf{r}')}{N} d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (70)$$

$$\eta = \frac{\partial^2 E}{\partial N^2} = \int \eta(\mathbf{r}) \frac{\partial \rho(\mathbf{r})}{\partial N} d\mathbf{r} = \int \eta(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} \quad (71)$$

The two definitions of the local hardness given in eqs. (67) and (68) are different, because they use a different function as the weighting function, $f_1(\mathbf{r})$, of the hardness kernel. However, they integrate to an identical global hardness, so that one can write:

$$\iint \eta(\mathbf{r}, \mathbf{r}') \left[f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N} \right] d\mathbf{r}' d\mathbf{r} = 0 \quad (72)$$

which involves the deviation of the Fukui function from the average electron density per electron (the bracketed quantity), which is equal to $N\partial/\partial N[\rho/N]$, the derivative of the average density.¹⁷⁴

Far away from the nuclei, the leading term in the local hardness comes from the Coulombic contribution to the hardness kernel, so that:

$$\eta(\mathbf{r}) \simeq \int \frac{f_1(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (73)$$

with $f_1(\mathbf{r}')$, defined in eq. (66), being taken equal to $\rho(\mathbf{r})/N$. Then the local hardness becomes proportional to the electrostatic potential generated by the molecular charge distribution, as indicated in eq. (54).¹⁰³ Eq. (73) is an approximation of the Kohn–Sham potential derivative within the Hartree approximation, because it is an approximation of the screened local hardness, $\tilde{\eta}(\mathbf{r})$, introduced by Senet,¹⁰¹ which is the KS potential derivative with respect to N :

$$\tilde{\eta}(\mathbf{r}) = \left(\frac{\partial v_{KS}(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} = \int h_I(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}' \quad (74)$$

where the KS potential, $v_{KS}(\mathbf{r})$, is defined by:

$$v_{KS}(\mathbf{r}) = \mu - \frac{\delta T_S}{\delta \rho(\mathbf{r})} \quad (75)$$

T_S is the exact kinetic energy of a fictitious noninteracting electronic system having the same ground-state electronic density as the system

$$h_I(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_I[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (76)$$

where E_I is the sum of the Hartree–Coulomb repulsion energy, E_{Coul} , and of the exchange–correlation energy, E_{xc} [eq. (5)]. Here, again, h_I may have a different value if evaluated on the right or on the left of an integer number of electrons. This screened local hardness is indeed a new index of reactivity¹⁰¹ that is related to the global hardness, similar to $\eta(\mathbf{r})$ [eq. (50)] through:

$$\eta = \eta_F = \int \tilde{\eta}(\mathbf{r}) \rho_F(\mathbf{r}) d\mathbf{r} \quad (77)$$

where $\tilde{\eta}(\mathbf{r})$ is given by eq. (74), ρ_F is the frontier orbital density; that is, the HOMO or LUMO density for the left or right derivative, respectively, according to eq. (35). The local hardness can then be related to the screened local hardness:

$$\eta(\mathbf{r}) = \int h_I(\mathbf{r}, \mathbf{r}') \rho_F(\mathbf{r}') d\mathbf{r}' \quad (78)$$

which differs from eqs. (67) and (68) by both the kernel and the weighting function. Expressing $h_I(\mathbf{r}, \mathbf{r}')$ as a sum of a Hartree–Coulomb contribution and an exchange–correlation, one obtains¹⁰¹:

$$\tilde{\eta}(\mathbf{r}) = \int \frac{\rho_F(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int h_{Ixc}(\mathbf{r}, \mathbf{r}') \rho_F(\mathbf{r}') d\mathbf{r}' \quad (79)$$

Far away from the nuclei, the exchange–correlation contribution can be neglected, allowing recovery of a new form for eq. (73):

$$\eta(\mathbf{r}) \simeq \int \frac{\rho_F(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (80)$$

This formula was given by Ghanty and Ghosh¹⁷⁵ and rederived by Senet.¹⁰¹

Berkowitz, Ghosh, and Parr established in 1985¹⁷⁶ that the functional derivative, $(\delta\mu/\delta\rho(\mathbf{r}))_{v(\mathbf{r})}$, is ambiguous, because, for a ground state, $\rho(\mathbf{r})$ and $v(\mathbf{r})$ are dependent according to the Hohenberg–Kohn theorem,³ which states that $v(\mathbf{r})$ is completely determined by $\rho(\mathbf{r})$. Harbola, Chattaraj, and Parr⁶⁴ showed that one can add any arbitrary function, $\lambda(\mathbf{r})$, to the Fukui function:

$$f(\mathbf{r}) = \left(\frac{\delta\mu}{\delta v(\mathbf{r})} \right)_{\rho(\mathbf{r})} + \lambda(\mathbf{r}) \quad (81)$$

so that the corresponding local hardness is given by:

$$\left(\frac{\delta\mu}{\delta\rho(\mathbf{r})} \right)_{v(\mathbf{r})} = \eta + \int \lambda(\mathbf{r}') \frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})} d\mathbf{r}' \quad (82)$$

Taking $\lambda(\mathbf{r}) = 0$, one gets:

$$\eta = \left(\frac{\delta\mu}{\delta\rho(\mathbf{r})} \right)_{v(\mathbf{r})} \quad (83)$$

that is, eq (43), so that one gets both equations [compare to eqs. (67) and (68)]:

$$\eta = \eta(\mathbf{r}) = \int f(\mathbf{r}') \eta(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (84)$$

$$\eta = \iint f(\mathbf{r}) f(\mathbf{r}') \eta(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (85)$$

Because Fukui functions are involved, and related to the ground-state densities, $f(\mathbf{r}')$ rejects all but the N -dependence associated with a change in the density, $\rho(\mathbf{r}')$. This is no longer true for all states, except for the ground state. Defined in such a way, the local hardness is constant and plays a less important role in reactivity studies. On the contrary, softness carries much more information.

Because of the discontinuities in derivatives in finite systems, one can define three different types of hardness kernels for electrophilic, nucleophilic, and radical attacks in analogy with the corresponding Fukui functions.¹³⁰

C. LINEAR RESPONSES

Conventional linear response. The conventional linear (density–density) response function¹⁷⁷ is:

$$\chi_1(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')} \right)_N \quad (86)$$

It is connected to the softness functions, because Berkowitz and Parr¹²⁴ proved the following relation

$$\begin{aligned} \chi_1(\mathbf{r}, \mathbf{r}') &= \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')} \right)_N = -s(\mathbf{r}, \mathbf{r}') + \frac{s(\mathbf{r})s(\mathbf{r}')}{S} \\ &= -s(\mathbf{r}, \mathbf{r}') + f(\mathbf{r})s(\mathbf{r}') \end{aligned} \quad (87)$$

The Berkowitz–Parr equation [eq. (87)] shows that the chemical reactivity, as measured by the softness kernel, is the sum of two contributions: (i) the (nonlocal) response function of the system that contains contributions of all the MOs to the reactivity; and (ii) the electronic reactivity contained in the local softness, which is dominated by the frontier orbitals as seen in the frozen-orbitals approximation [eq. (34)]. This shows that the polarization changes in the electronic distribution (response to the external potential displacements) can be determined from the softness properties calculated for the fixed nuclear geometry (external potential).

Cohen and coworkers¹⁷⁸ generalized the expressions (60) and (64) for gapless solid state (i.e., infinitely soft) systems, and established a relationship between the dielectric function of many-body perturbation theory and the softness kernel.

Senet discussed extensively the properties of the response functions in refs. 61 and 62. He showed⁶¹ that the Fukui functions can be related to the linear response, $\chi_1(\mathbf{r}, \mathbf{r}_1)$, of the system to a change of the external potential through the relation:

$$f(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'') + \int \chi_1(\mathbf{r}, \mathbf{r}') \eta(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' \quad (88)$$

where $\eta(\mathbf{r}', \mathbf{r}'')$ is the symmetric hardness kernel related to the hardness, η , by eq. (84), and that any normalized function $\tau(\mathbf{r})$ satisfies:

$$f(\mathbf{r}) = \tau(\mathbf{r}) + \int \int \chi_1(\mathbf{r}, \mathbf{r}'') \eta(\mathbf{r}', \mathbf{r}'') \tau(\mathbf{r}') d\mathbf{r}' d\mathbf{r}'' \quad (89)$$

Linear response at constant chemical potential. The linear density–density response function at con-

stant chemical potential:

$$\chi_1^\mu(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')} \right)_\mu \quad (90)$$

is nothing (to a minus sign), but the softness kernel as defined in eq. (60). It may play an important role when a system is constrained by a given value of the chemical potential. This is, for instance, the case of electrochemical systems where the scalar, global (i.e., space independent), chemical potential may be fixed. In that case we have:

$$\begin{aligned} \delta \rho(\mathbf{r}) &= \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right) \delta \mu + \int \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')} \right)_\mu \delta v(\mathbf{r}') d\mathbf{r}' \\ &= S f(\mathbf{r}) \delta \mu + \int \chi_1^\mu(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') d\mathbf{r}' \end{aligned} \quad (91)$$

The second term in this equation describes the distortion of the electronic density at constant number of electrons under its polarization. If this equation is integrated over \mathbf{r} , one gets the change in the electron number driven by the value of the chemical potential, $\delta N = S \delta \mu$, because $f(\mathbf{r})$ is normalized [eq. (52)] and Bureau and Lecayon showed that, at the LSD level of approximation, integral over \mathbf{r} of the second term in eq. (91) is zero.¹⁷⁹

Definition of local functions involving the linear response. An integral form for the definition of the Fukui function [eq. (34)] has also been given:

$$f^\alpha(\mathbf{r}) = \int K^{-1}(\mathbf{r}, \mathbf{r}') \sum_\sigma |\psi_F^\alpha(\mathbf{r}, \sigma)|^2 d\mathbf{r}' \quad (92)$$

with K^{-1} being the reciprocal kernel of the potential response function introduced by Cohen^{178,180}:

$$\begin{aligned} K(\mathbf{r}, \mathbf{r}') &= \frac{\partial v(\mathbf{r}')}{\partial v_{KS}(\mathbf{r})} \\ &= \delta(\mathbf{r} - \mathbf{r}') - \int \chi_{1\sigma}^\mu(\mathbf{r}, \mathbf{r}'') h_1(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \end{aligned} \quad (93)$$

where $\chi_{1\sigma}^\mu(\mathbf{r}, \mathbf{r}'')$ is the linear density–density response evaluated at constant potential μ for spin σ [eq. (90)]. Senet established a strong relationship between eq. (93) and eq. (89); that is, inverting eq.

(93) one gets:

$$\begin{aligned} K^{-1}(\mathbf{r}, \mathbf{r}') &= \frac{\partial v_{KS}(\mathbf{r})}{\partial v(\mathbf{r}')} \\ &= \delta(\mathbf{r} - \mathbf{r}') + \int \chi_{I\sigma}^{\mu}(\mathbf{r}, \mathbf{r}'') h_I(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \end{aligned} \quad (94)$$

Making use of eq. (93), Senet⁶² showed that eqs. (34) and (92) are identical. Accordingly, the Fukui functions are screened frontier orbitals approximated by the frontier orbitals in case of unpolarizable electrons approximation ($\chi_1 = 0$) or noninteracting electrons approximation ($h_I = 0$). Similarly, local softness, $s(\mathbf{r})$, is equal to a screened LDOS at the Fermi level.^{180, 178, 101}

Using eqs. (74), (76), and (77), one gets:

$$\begin{aligned} \eta &= \int \rho_F(\mathbf{r}) \tilde{\eta}(\mathbf{r}) d\mathbf{r} \\ &= \iiint \rho_F(\mathbf{r}'') \rho_F(\mathbf{r}) K^{-1}(\mathbf{r}, \mathbf{r}') h_I(\mathbf{r}', \mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \end{aligned} \quad (95)$$

which establishes that the hardness is equal to the screened electron–electron interaction energy between the frontier orbital densities.

Nonlinear responses. Nonlinear response functions, χ_n (i.e., high-order perturbations), will not be discussed here. We simply mention that relations connecting them to Fukui responses, $\xi(\mathbf{r}, \mathbf{r}')$, exist (see Table I), and they have been discussed by Fuentealba and Parr¹⁸¹ for molecular systems, and more generally by Senet.^{61, 62}

D. HSAB PRINCIPLE REVISITED

Li and Evans¹⁸² showed recently that both frontier orbitals theory and the HSAB principle are strongly related to the Fukui functions. For this purpose, they used the energy expansion up to second order in the changes, ΔN and $\Delta v(\mathbf{r})$:

$$\begin{aligned} \Delta E &= \mu \Delta N + \frac{1}{2} \eta \Delta N^2 + \int \rho(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \\ &+ \Delta N \int f(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \\ &+ \frac{1}{2} \int \left(\frac{\partial \rho(\mathbf{r})}{\partial v(\mathbf{r}')} \right)_N \Delta v(\mathbf{r}) \Delta v(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (96)$$

in which all the terms have been defined previously. To express eq. (96) in terms of local and

global functions, Li and Evans used eq. (87), proposed by Berkowitz and Parr¹²⁴ for the differential density–density response function $[\partial \rho(\mathbf{r}) / \partial v(\mathbf{r}')]$, and they assumed that the softness kernel could be approximated by a linear combination of a local part and a nonlocal part:

$$s(\mathbf{r}, \mathbf{r}') = as(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') + b \frac{s(\mathbf{r})s(\mathbf{r}')}{S} \quad (97)$$

with $a + b = 1$. The particular case $a = 1$ (local model) is the approximation of the softness kernel proposed by Vela and Gázquez.¹⁰⁰ One gets¹⁸²:

$$\begin{aligned} \Delta E &= \mu \Delta N + \frac{1}{2} \eta \Delta N^2 + \int \rho(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \\ &+ \Delta N \int f(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \\ &+ \frac{a}{2} \eta \left(\int s(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r} \right)^2 \\ &- \frac{a}{2} \int s(\mathbf{r}) (\Delta v(\mathbf{r}))^2 d\mathbf{r} \end{aligned}$$

The chemical reactivity and the selectivity can be described by using this model. Let us consider the interaction of two molecules, i and j ; one can express the energy perturbations at the beginning of a reaction when two molecules, i and j are approaching each other by:

$$\begin{aligned} \Delta E &= \Delta E_i + \Delta E_j \\ &= \Delta E_I + \Delta E_{II} + \Delta E_{III} + \Delta E_{IV} + \Delta E_V + \Delta E_{nn} \end{aligned} \quad (98)$$

where:

$$\begin{aligned} \Delta E_I &= (\mu_i - \mu_j) \Delta N + \frac{1}{2} (\eta_i + \eta_j) \Delta N^2 \\ \Delta E_{II} &= \int (\rho_i(\mathbf{r}) \Delta v_i(\mathbf{r}) + \rho_j(\mathbf{r}) \Delta v_j(\mathbf{r})) d\mathbf{r} \\ \Delta E_{III} &= \Delta N \int (f_i(\mathbf{r}) \Delta v_i(\mathbf{r}) - f_j(\mathbf{r}) \Delta v_j(\mathbf{r})) d\mathbf{r} \\ \Delta E_{IV} &= \frac{a\eta_i}{2} \left(\int s_i(\mathbf{r}) \Delta v_i(\mathbf{r}) d\mathbf{r} \right)^2 \\ &+ \frac{a\eta_j}{2} \left(\int s_j(\mathbf{r}) \Delta v_j(\mathbf{r}) d\mathbf{r} \right)^2 \\ \Delta E_V &= \frac{a}{2} \int (s_i(\mathbf{r}) (\Delta v_i(\mathbf{r}))^2 + s_j(\mathbf{r}) (\Delta v_j(\mathbf{r}))^2) d\mathbf{r} \end{aligned}$$

E_{nn} is the nuclear–nuclear repulsion energy, and $\Delta N = \Delta N_i = -\Delta N_j \geq 0$. The ΔE_I term describes the role of global parameters (i.e., reactivity of the molecules): From the first term of ΔE_I , one can deduce that the reaction is greatly favored by a large difference in chemical potential and a large electron transfer. The second term in ΔE_I indicates that the reaction is favored by small hardness values. In other words, soft molecules are more reactive.

The selectivity is driven by the local parameters, involved in the ΔE_{II-V} terms. ΔE_{II} as well as ΔE_{nn} are terms that contribute to the reactivity of molecules, taking into account the changes in geometry during the reaction. The other terms are related to the frontier orbitals, which concern more the beginning of the reaction.

If one considers the case of a small electron transfer (i.e., small ΔE_{III}), ΔE_{IV} is a term that is always positive so that one should have a local softness value as small as possible, provided the ΔE_V is smaller than ΔE_{IV} . This is true when the hardnesses, η_i , are large. In this way, one obtains the first part of the HSAB principle: *hard like hard*. When the global hardnesses, η_i , are small, the reactivity is determined by ΔE_V , so that the reaction center is located at the site of maximal softness. In this case, the reaction will occur between the softer sites of soft molecules, according to the second part of the HSAB principle: *soft like soft*.

Finally, one must consider the case in which electron transfer occurs; that is, ΔE_{III} is the dominant term. In that case, one can split the change in the potential, $\Delta v_i(\mathbf{r})$, into a nuclear part and an electronic part. The nuclear part can be approximated by:

$$\Delta v_i^{nuc}(\mathbf{r}) \approx \sum_{k \in j} \frac{q_{jk} \Delta R_{jk}(\mathbf{r})}{(R_{jk}^0(\mathbf{r}))^2} \quad (99)$$

where q_{jk} are charges of atom k in molecule j , $R_{jk}^0(\mathbf{r})$ is the distance between atom k in molecule j and position \mathbf{r} of molecule i before the change, and $\Delta R_{jk}(\mathbf{r})$ the change of the corresponding distance. When two molecules approach each other, $\Delta R_{jk}(\mathbf{r})$ is negative. The electronic part, due to electron transfer between molecules i and j , may be approximated by:

$$\Delta v_i^{elec}(\mathbf{r}) \approx \sum_{k \in j} \frac{\Delta N_{jk}}{R_{jk}(\mathbf{r})} \quad (100)$$

where ΔN_{jk} is the change in the number of electrons of atom k in molecule j . Using approxima-

tions (99) and (100) for E_{III} of eq. (98), one gets two contributions:

$$\int f_i(\mathbf{r}) \left(\sum_{k \in j} \frac{q_{jk} \Delta R_{jk}(\mathbf{r}) \Delta N_i}{(R_{jk}^0(\mathbf{r}))^2} \right) + \int f_j(\mathbf{r}) \left(\sum_{l \in i} \frac{q_{il} \Delta R_{il}(\mathbf{r}) \Delta N_j}{(R_{il}^0(\mathbf{r}))^2} \right) \quad (101)$$

which are positive terms for reactions between two oppositely charged molecules for which one can expect $q_{jk} * \Delta N_i < 0$ and $q_{il} * \Delta N_j < 0$. If charges are large, this term is a large and positive one, so that one has to minimize the Fukui function to allow the reaction to proceed. If the charges are small, the dominant terms are:

$$\int f_i(\mathbf{r}) \left(\frac{\Delta N_{jk} \Delta N_i}{R_{jk}(\mathbf{r})} \right) d\mathbf{r} + \int f_j(\mathbf{r}) \left(\frac{\Delta N_{il} \Delta N_j}{R_{il}(\mathbf{r})} \right) d\mathbf{r} \quad (102)$$

and because $\Delta N_i * \Delta N_j < 0$, the Fukui function must be maximized on the preferred sites for the reaction.

VI. Other Concepts

A. SHAPE OF ELECTRONIC DENSITY

The shape of the electronic density is defined as the ratio of the density to the number of electrons:

$$\rho(\mathbf{r}) = N\sigma(\mathbf{r}) \quad (103)$$

$\sigma(\mathbf{r})$ (not to be confused with the spin index) is called the shape factor and was introduced by Parr and Bartolotti in 1983.¹⁸³ The contribution of the shape of a system to the electronegativity and hardness has been investigated recently.^{65,136} One has:

$$\int \sigma(\mathbf{r}) d\mathbf{r} = \frac{1}{N} \int \rho(\mathbf{r}) d\mathbf{r} = 1 \quad (104)$$

and one can choose to replace variable ρ by N and σ :

$$d\rho(\mathbf{r}) = \sigma(\mathbf{r}) dN + N d\sigma(\mathbf{r}) \quad (105)$$

Constant σ changes are called isomorphic.⁶⁵ Similar Euler equations to eqs. (4) and (72) and fluctuation formulas can be derived for isomorphic en-

sembles as for canonical ensembles. Using:

$$\begin{aligned} \left(\frac{\partial \sigma(\mathbf{r})}{\partial N} \right)_v &= \frac{\partial}{\partial N} \left(\frac{\rho(\mathbf{r})}{N} \right)_v \\ &= \frac{1}{N} \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v - \frac{1}{N^2} \rho(\mathbf{r}) \\ &= \frac{1}{N} \left(f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N} \right) \end{aligned} \quad (106)$$

and the identity:

$$\left(\frac{\partial E}{\partial N} \right)_v = \left(\frac{\partial E}{\partial N} \right)_\sigma + \int \left(\frac{\delta E}{\delta \sigma(\mathbf{r})} \right)_N \left(\frac{\partial \sigma(\mathbf{r})}{\partial N} \right)_v d\mathbf{r} \quad (107)$$

one can obtain, for electronegativity¹³⁶:

$$\chi_v = \chi_\sigma - \frac{1}{N} \int \left(\frac{\delta E}{\delta \sigma(\mathbf{r})} \right)_N \left(f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N} \right) d\mathbf{r} \quad (108)$$

This equation shows that the electronegativity at constant external potential, χ_v , can be expressed as the sum of the electronegativity at a constant shape factor, χ_σ , and a term describing the effect on the energy caused by a shape factor change at a constant number of electrons. The shape factor plays an important role in the study of molecular similarity.¹⁸⁴ For instance, a quite common index of similarity (here labeled Ω) of molecules A and B may be written as:

$$\Omega(A, B) = \frac{\int \sigma_A(\mathbf{r}) \sigma_B(\mathbf{r}) d\mathbf{r}}{(\int \sigma_A^2(\mathbf{r}) d\mathbf{r})^{1/2} (\int \sigma_B^2(\mathbf{r}) d\mathbf{r})^{1/2}} \quad (109)$$

involving only shape factors, but which can be equivalently expressed as:

$$\Omega(A, B) = \frac{\int \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) d\mathbf{r}}{(\int \rho_A^2(\mathbf{r}) d\mathbf{r})^{1/2} (\int \rho_B^2(\mathbf{r}) d\mathbf{r})^{1/2}} \quad (110)$$

B. NUCLEAR FUKUI FUNCTIONS

Nuclear Fukui functions are defined by^{178, 180, 185}:

$$\phi_\alpha = - \int f(\mathbf{r}) \left(\frac{\delta v(\mathbf{r})}{\delta \mathbf{R}_\alpha} \right)_N d\mathbf{r} = \left(\frac{\partial \mathbf{F}_\alpha}{\partial N} \right)_v = \left(\frac{\partial \mu}{\partial \mathbf{R}_\alpha} \right)_N \quad (111)$$

where \mathbf{R}_α is the nuclear coordinate of atom α , and \mathbf{F}_α is the force on nucleus α . They constitute the conformal contribution to a change in the elec-

tronic chemical potential because we can write, considering a change of the chemical potential of the system in the canonical ensemble $\mu = \mu[N, v]$:

$$d\mu = \eta dN + \int f(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r} \quad (112)$$

replacing $dv(\mathbf{r})$ by:

$$\sum_\alpha \left(\frac{\delta v(\mathbf{r})}{\delta \mathbf{R}_\alpha} \right)_N d\mathbf{R}_\alpha$$

one gets:

$$d\mu = \eta dN - \sum_\alpha \phi_\alpha d\mathbf{R}_\alpha \quad (113)$$

Within the canonical ensemble, one has the following fluctuation formula for ϕ :

$$\phi_\alpha = \frac{1}{k_B T} (\langle \mathbf{F}_\alpha \cdot \mu \rangle - \langle \mathbf{F}_\alpha \rangle \langle \mu \rangle) \quad (114)$$

which shows that the nuclear Fukui function measures local force fluctuations on nucleus α . Baeckelandt¹⁸⁵ discussed the relationships between nuclear Fukui functions, Berlin's binding function,¹⁸⁶ and geometrical indices⁶⁵ within the isomorphic ensemble.

C. MOLECULAR CHARGE SENSITIVITY ANALYSIS

Nalewajski introduced a quite general analysis of molecular interactions in the hardness and softness representations, which have been defined at different levels of partitioning (resolution) of molecular systems. Electronic population was then considered at the local level, (i.e., density), atoms in molecules (AIM) resolution, group (larger molecular fragments), or the total number of electrons (global resolution), each variable being defined within this resolution degree. Interestingly, it can also be defined at a molecular orbital level of partitioning (orbitally resolved theory).¹⁸⁷ At local resolution, and to a lesser extent at AIM resolution, the electronic distribution is totally "frozen" (i.e., constrained), whereas it is totally relaxed at the global level of resolution. At each of these levels of resolution, one can define the energy functional, a chemical potential, a hardness or a softness, which are summarized synthetically in Table III. Full tables of definitions and relations may be found in ref. 187. The use of the chain rule transformation of derivatives allows one to obtain

TABLE III.
Potentials, Derivatives and Differentials in
Hardness (Interaction) and
Softness (Response) Representations.^a

Hardness (interaction) representation

Potential: $E[\tilde{n}_x] = F[\tilde{n}_x] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$

Chemical potential: $\mu_x = \frac{\partial E[\tilde{n}_x]}{\partial \tilde{n}_x}$

Second derivatives: $\eta_x = \frac{\partial^2 E[\tilde{n}_x]}{\partial \tilde{n}_x \partial \tilde{n}_x}$

Softness (response) representation

Potential: $\Omega[\tilde{\mu}_x] = E - \tilde{\mu}_x n_x$

Population and first differential: $n_x = \frac{\partial \Omega[\tilde{\mu}_x]}{\partial \tilde{\mu}_x}$

Softness and second derivatives: $s_x = \frac{\partial^2 \Omega[n_x]}{\partial \tilde{\mu}_x \partial \tilde{\mu}_x}$

^a \tilde{n}_x may represent either N (global), N_G (group), N_{AIM} (AIM), n (MO occupation), or $\rho(\mathbf{r})$ (local). Corresponding differentials include global hardness or softness ($\tilde{n}_x = N$), hardness or softness kernels (local), and hardness or softness matrices (others) and $\tilde{\mu}_x$ may be global hardness or softness ($\tilde{\mu}_x = \mu$), hardness or softness kernels (local), hardness or softness matrices (others), or $\mu_{MO} = \epsilon_i$.

combination rules between more or less local properties (mixed resolution derivatives); for instance:

$$\eta^{AIM} = \frac{\partial^2 E}{\partial N \partial N^{AIM}} = \frac{\partial \mu^{AIM}}{\partial N} = \frac{\partial \mu}{\partial N^{AIM}} = \left(\frac{\partial \mu}{\partial N} \right) \left(\frac{\partial N}{\partial N^{AIM}} \right) = \eta \cdot 1 \quad (115)$$

where the superscript AIM indicates a group or atom fragment (AIM) in equilibrium with its system remainder. At AIM resolution, each isolated fragment bears an effective charge, q_i , so that a knowledge of the isolated atom hardness, η^0 , enables one to calculate first-order corrections to the isolated atom chemical potential, μ_i^0 , according to $\mu_i(q_i) \approx \mu_i^0 - q_i \eta_i^0$.

Charge sensitivity analysis has been used for the description of charge rearrangements between complex reactants in various examples of reactivity and catalysis, as summarized in Nalewajski et al.'s review.¹⁸⁸ As just mentioned, Nalewajski¹⁸⁷ introduced, in particular, the MO resolution based on the MO occupation numbers, which can be considered as a phenomenological description of the internal polarization of molecular states.¹⁸⁹ Some calculations related to atomic orbital electronegativities and hardnesses are discussed in ref. 81.

The chemical hardness matrix (or orbitally resolved hardness tensor) was introduced by Teter¹⁹⁰ and it measures the first-order change of an eigenvalue caused by a first-order variation of its occupation number, the total number of electrons being allowed to vary. Indeed it can be traced back to Slater's pioneer work within the X-alpha method for which he proposed the Taylor expansion of the total energy with respect to the occupation numbers.¹⁹¹ The elements of this matrix are given by:

$$\eta_{ij} = \frac{\partial E[\rho]}{\partial n_i \partial n_j} = \frac{\partial \epsilon_i}{\partial n_j} \quad (116)$$

where n_j is the occupation number of orbital j of eigenvalue ϵ_j .

Applying the Hellman–Feynman theorem to the definition [eq. (116)], one obtains:

$$\begin{aligned} \eta_{ij} &= \langle \psi_i | \frac{\partial}{\partial n_j} [T + V_{ion} + V_{hxc}] | \psi_i \rangle \\ &= \langle \psi_i | \frac{\partial V_{hxc}}{\partial \rho} \frac{\partial \rho}{\partial n_j} | \psi_i \rangle \end{aligned} \quad (117)$$

where V_{hxc} is the Hartree and exchange-correlation potential.

The term, $\partial \rho / \partial n_j$, contains two parts: (i) the change of the screening potential with a variation of the occupation number for frozen orbitals; and (ii) the relaxation of the wave function.¹⁹² The hardness matrix has been generalized to nondiagonal occupation number¹⁹² and proposed as an additional condition for transferability (i.e., feature of quality) for the elaboration of (norm-conserving) pseudopotentials.^{190, 193}

Grigorov et al.^{194, 195} recently proposed an efficient numerical scheme to evaluate hardness tensor elements from their definition [eq. (116)], and they applied it to water and ferrocene systems.¹⁹⁵ Following Nalewajski¹⁹⁶ and Liu,¹⁹⁷ they suggested that these orbitally resolved hardness tensor elements are a measure of the interaction of electrons belonging to the two corresponding MOs and the diagonal elements are a measure of the self-interaction energy. Channels of reactivity may be described by what Nalewajski called the normal (spin)orbitals^{189, 196, 198}; that is, the eigenvectors of the hardness tensor, which can be determined easily through a diagonalization. These channels account for the polarization of the electron density at the early stages of the chemical reactions. See also refs. 199, 200.

VII. Gap Discontinuity Problem

A. DISCONTINUITY IN $\partial E/\partial N$

For systems possessing a HOMO–LUMO gap, the discontinuity in the $\partial E/\partial N$ was evidenced by Perdew and coworkers in 1982,¹³² and has also been discussed by Almbladh and von Barth²⁰¹ and Parr and Bartolotti.¹⁸³ It has been assumed that, as a consequence of the Pauli principle, these derivatives, including the chemical potential itself, are not well defined. The discontinuity in the $\partial E/\partial N_S$ function has been established by Galvan and Vargas.¹⁶⁹ [N_S is defined in eq. (56).]

For finite systems with an energy gap, $\mu(N)$ is a step function, constant between jumps at integral values of N . Accordingly, if N is not considered as a continuous variable, as Janak did,²⁰² or through the use of an ensemble, as discussed in section IIIC, both $(\partial N/\partial \mu)_{v(r)}^\alpha$ and $(\partial \rho(r)/\partial \mu)_{v(r)}^\alpha$, either vanish or do not exist, with $\alpha = +, -, \text{ or } 0$ as in eqs. (29)–(31). In these conditions, local and global softnesses are not well defined in systems like molecules (with discrete energy levels) or insulators, whereas Fukui functions are still meaningful. The significance of the HOMO is still an object of controversy.²⁰³ Nesbet²⁰⁴ recently stressed that the discontinuity is a direct consequence of the Fermi statistics, but this did not imply any derivative discontinuity in the energy functionals for unconstrained variations of the electronic density, whereas Perdew and Levy considered that the constraint is included in the variational determination of the energy.^{205,206} The consequences of this discontinuity for the meaning of the energy levels was investigated by Russier.²⁰⁷ The consistency between the fractional number formalism and the ensemble approach was established by Casida.²⁰⁸

Therefore, $\partial E/\partial N$ may have different values when evaluated to the left or the right of an integral number of electrons. These derivations correspond to the response of the electrons to an electrophilic ($\Delta N < 0$) or nucleophilic ($\Delta N > 0$) perturbation, respectively. Because of the larger impact of the discontinuity into the second derivative, this fact has been fully included in the definition of local properties such as Fukui functions (*vide infra*, section IVA), whereas it has been mostly neglected in the estimation of electronegativity. In fact, this neglect concerns third-order terms because second-order terms do cancel.²⁰⁹ Parr and Pearson's general definition of atomic hardness as

a derivative does not make a distinction between acidic and basic behavior of atoms, because it is taken as the curvature of the $E = f(N)$ function for the neutral atom. If one assumes that $\mu(N)$ is a step function, left and right derivatives are zero. Komorowski^{97,210} proposed to take averages of hardness of neutral and negatively charged, or neutral and positively charged, atoms for an acidic or basic hardness, respectively. In the same vein, Chattaraj et al.¹³⁰ pointed out that three different types of hardness kernels may be defined, and Gálvan et al. considered different hardnesses according to the sign of the charge transfer for a Si_4 cluster.²¹¹

B. FOR A MORE ACCURATE DETERMINATION OF χ

As just mentioned, for any isolated species, Perdew et al. showed that derivatives with respect to N are different, depending on whether N increases or decreases. Neglecting the spin polarization (see section IVE), one has $\mu = \epsilon_{\text{SOMO}}$, the energy of the semioccupied molecular orbital, in case of open-shell molecules, but for a closed-shell isolated system with frozen density, $\mu = (\partial E/\partial N)_v = \mu(N)$, is a step function, constant between jumps at integral values of N_0 . Hence, one gets significantly different values according to the side from which the derivative is made. It is customary to take the average of the two derivatives (as in case of the finite difference approximation, etc.), but this assumes that the relaxations of the electronic system during the electron attachment or detachment processes have the same amplitude.

Therefore, because of the convexity of the $E(N)$ function,¹²⁴ one can expect that, at nonzero temperatures, the chemical potential should not lie exactly in the middle of the gap. Its position may depend, on the one hand, on the densities of states of both the valence band and conduction band near the edge (i.e., number of molecular orbitals that have energies close to the HOMO and LUMO energies. On the other hand, it depends on the temperature, a parameter usually neglected by most calculations (except for dynamics), supposed to be performed at 0 K.

Cohen²¹² proved that the DF on which the ensemble KS theory is based does not exist at $T = 0$, so that reactivities should be "violently" temperature-dependent for $k_B T \ll \eta$, with η being the energy gap of the system.

To locate properly the chemical potential, μ , Grigorov et al. recently proposed a technique mak-

ing use of statistical thermodynamics at finite temperature. They performed calculations in which they showed that, through an ensemble system, the chemical potential can be calculated from a self-consistent calculation performed with ground-state molecular orbitals and populated following the Fermi–Dirac statistics at finite temperature T .¹⁹⁴ The algorithm consists of the following steps:

1. Initialize occupation numbers n_i .
2. For this given occupation number set, calculate the total energy and eigenvalue spectrum ϵ_i .
3. Determine the chemical potential μ as the solution of the equation conserving the number of electrons:

$$N - \sum_i \frac{1}{1 + \exp(\beta(\epsilon_i - \mu))} = 0$$

with the symbols already defined in Section IVC in this work.

4. Recalculate the occupation numbers, applying the Fermi statistics:

$$n_i = \frac{1}{1 + \exp(\beta(\epsilon_i - \mu))}$$

5. If self-consistency is not reached in μ , go to step 2.

Usually, self-consistency in the occupation numbers and in μ is reached within a few iterations.²¹³

VIII. Concluding Remarks

The main conclusions of the present article are as follows:

- Whereas conceptual DFT has introduced many reactivity descriptors, which are inter-related, as reviewed in this study, there is interest in performing DFT calculations for this purpose. In other words, it is recommended to use what Parr and Yang⁶ called “calculational DFT”) in place of HF or semi-empirical calculations for the computation of first-order (μ) or second-order reactivity properties (e.g., Fukui functions).
- The interest in topological partitioning of molecular space for the calculation of atomic properties like condensed Fukui functions,

as has been known for a long time for charges, is reinforced.

- The limitation of the finite difference approximation in the calculation of global properties such as electronegativity and hardness is emphasized. An algorithm is given to extract the chemical potential (i.e., the electronegativity from a direct use of the Euler equation of KS equations), justified by an ensemble description of the electronic system at finite temperature.
- The importance of spin polarization has not yet been investigated sufficiently.

The softness and hardness kernels represent a nonlocal response to a local static perturbation, and are a first attempt to describe reactivity, whereas, in real chemical systems, the perturbation comes from a second (dynamic) subsystem and not a static potential. Further work is needed for better description of reactivity, by introducing, for instance, dynamical response functions.

All the concepts discussed in this article have been derived from an energy perturbation scheme. Recently, another kind of energy expansion, the functional expansion, was proposed by Parr, Liu, and coworkers.^{214, 215} It is worth noting that, whereas the same concepts as those gathered in Tables I and II have been derived, the sign and coefficients in the energy expansions may differ. More insight into the relationships between the various indices will be gained in future investigations.

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